Oxygen-Converter Reduction of Iron and Manganese from Their Oxides by Components Dissolved in Liquid Iron

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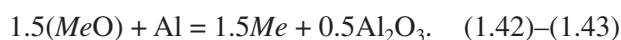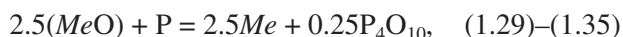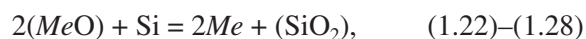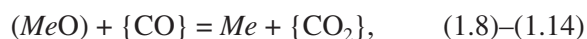
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Thermodynamic analysis of the reduction of iron and manganese from their oxides in steel-smelting on the basis of tabular data was undertaken for the reaction of pure components in [1]. The basic thermodynamic function of reduction—the standard change in Gibbs energy on oxide formation—was calculated for all steel-smelting temperatures. All seven iron and manganese oxides that are stable at those temperatures were considered; Fe_2O_3, Fe_3O_4, FeO and MnO_2, Mn_2O_3, Mn_3O_4, MnO. Potential reducing agents were divided into three groups: traditional reducing agents (solid carbon C_{so}, carbon monoxide CO, hydrogen H_2); hot-metal impurities ([C], [Si], [P], and even [Fe], which is a reducing agent for manganese); and reducing agents (C_{so}, Si, Mn, Al, and Ca).

This classification proves valid. In fact, reactions with traditional reducing agents have been extensively studied; the reducing agents ensure practically complete reduction of iron and manganese from their oxides, even those that are most resistant to reduction (such as FeO and MnO). Hot-metal impurities may offer a unique opportunity to combine processes: for example, the removal of a harmful impurity (phosphorus) and the reduction of iron from ferrous oxide FeO.

All possible reactions of the seven iron and manganese oxides with all the reducing agents were systematically considered in [1]. Allowing for the possible transformations of the reducing agents, we find that there are 43 possible reactions.[1]

$$(MeO) + C_{so} = Me + \{CO\}, \quad (1.1)–(1.7)$$

$$(MeO) + \{CO\} = Me + \{CO_2\}, \quad (1.8)–(1.14)$$

$$(MeO) + \{H_2\} = Me + \{H_2O\}, \quad (1.15)–(1.21)$$

$$2(MeO) + Si = 2Me + (SiO_2), \quad (1.22)–(1.28)$$

$$2.5(MeO) + P = 2.5Me + 0.25P_4O_{10}, \quad (1.29)–(1.35)$$

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[1] The numbers of these reactions correspond to their numbers in [1]. The first figure (before the decimal point) identifies the literature source; the second (after the point) is the number of the reaction in that source. Equations whose number does not include a decimal point originate in this article, rather than in a literature source.

$$(Mn_nO_m) + Fe = Mn + FeO, \quad (1.36)–(1.39)$$

$$(MeO) + Ca = Me + CaO, \quad (1.40)–(1.41)$$

$$1.5(MeO) + Al = 1.5Me + 0.5Al_2O_3. \quad (1.42)–(1.43)$$

Besides these 43 traditional reactions, two nontraditional reactions were considered in [1]: the reduction of FeO and MnO by carbon, to form CO_2

$$2(FeO) + C_{so} = 2Fe + CO_2, \quad (1.44)$$

$$2(MnO) + C_{so} = 2Mn + CO_2. \quad (1.45)$$
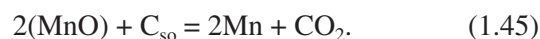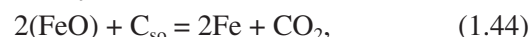
The reduction of iron and manganese from FeO and MnO, which is particularly difficult, is subjected to more detailed analysis in the present work, on the basis of [1].

SOLUTION OF ELEMENTS IN LIQUID IRON

The standard changes in Gibbs energy $\Delta_r G_j^\circ$ calculated in [1] from the tabular data of [2] will be denoted here by y_i: $\Delta_r G_j^\circ \equiv y_i$. (Here subscript i corresponds to the number of the reaction, and j to the number of the reducing agent.) In reality, the components are in solution, and hence we must take account of the transition of the basic components from the standard state to solution. This entails determining the corresponding change in Gibbs energy.

Note that the basic component of the metallic melt—iron—is essentially a solvent in dilute solution. Therefore, for the transition of the iron from the standard state to solution
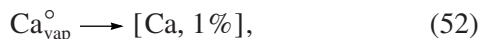
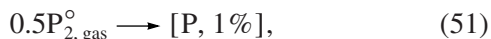$$Fe^\circ \longrightarrow [Fe, x_{Fe}]_{sol}, \quad (46)$$
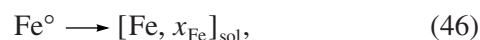
the change in Gibbs energy is
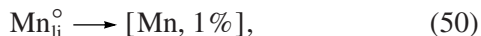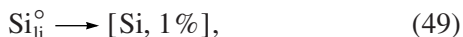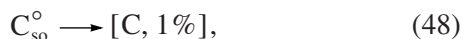
$$y_{46} \equiv \Delta G_{46} = RT \ln x_{Fe}, \quad (47)$$

where R is the universal gas constant; T is the absolute temperature; x_{Fe} is the mole fraction of iron in the liquid metal. (As a rule, $x_{Fe} \longrightarrow 1$ in hot metal and especially in steel.)

For the elements [C], [Si], [P], [Mn], [Ca], [Al], and others dissolved in liquid iron, which are potential

reducing agents, the state of a dilute solution with 1% of this component is regarded as the standard state. Then, for the solution of elements in liquid iron

$$C_{so}^{\circ} \longrightarrow [C, 1\%], \tag{48}$$

$$Si_{li}^{\circ} \longrightarrow [Si, 1\%], \tag{49}$$

$$Mn_{li}^{\circ} \longrightarrow [Mn, 1\%], \tag{50}$$

$$0.5P_{2,\,gas}^{\circ} \longrightarrow [P, 1\%], \tag{51}$$

$$Ca_{vap}^{\circ} \longrightarrow [Ca, 1\%], \tag{52}$$

$$Al_{li}^{\circ} \longrightarrow [Al, 1\%], \tag{53}$$

we may obtain formulas for the change in Gibbs energy on the basis of the results in [3]. Taking account of the equation $\Delta G_j = -2.3RT\log K_{p_j}$, we obtain the following formulas by recalculation of the relations $\log K_{p_j} = f_j(T)$ in [3] (where K_{p_j} is the equilibrium constant of the solution processes):

for the solution of graphite in liquid iron

$$y_{48} \equiv \Delta G_{48} = 22\,593.6 - 42.36T; \tag{54}$$

for the solution of silicon in liquid iron

$$y_{49} \equiv \Delta G_{49} = -131\,540 - 17.23T; \tag{55}$$

for the solution of manganese in liquid iron

$$y_{50} \equiv \Delta G_{50} = -4078 - 38.29T; \tag{56}$$

for the solution of phosphorus in liquid iron

$$y_{51} \equiv \Delta G_{51} = -122215 - 19.147T; \tag{57}$$
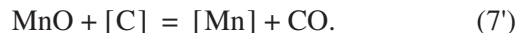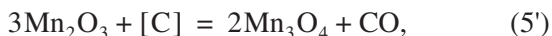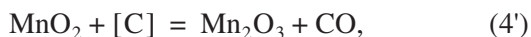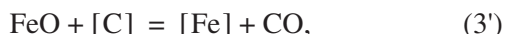
for the solution of calcium in liquid iron

$$y_{52} \equiv \Delta G_{52} = -39462 + 49.38T, \tag{58}$$

for the solution of aluminum in liquid iron

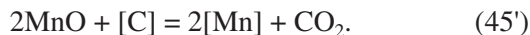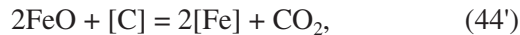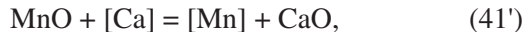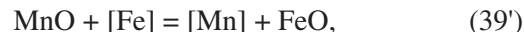$$y_{53} \equiv \Delta G_{53} = -63185 - 27.95T. \tag{59}$$

REACTIONS INVOLVING DISSOLVED COMPONENTS

Taking account of the solution of elements in liquid iron, we may rewrite Eqs. (1.1)–(1.45) for the reduction of iron and manganese in the following form, for the particular case of reduction by carbon dissolved in the metal [1]

$$3Fe_2O_3 + [C] = 2Fe_3O_4 + CO, \tag{1'}$$

$$Fe_3O_4 + [C] = 3FeO + CO, \tag{2'}$$

$$FeO + [C] = [Fe] + CO, \tag{3'}$$

$$MnO_2 + [C] = Mn_2O_3 + CO, \tag{4'}$$

$$3Mn_2O_3 + [C] = 2Mn_3O_4 + CO, \tag{5'}$$

$$Mn_3O_4 + [C] = 3MnO + CO, \tag{6'}$$

$$MnO + [C] = [Mn] + CO. \tag{7'}$$

The reduction of metal from the lowest oxides FeO and MnO by various reducing agents may be described by the following equations, retaining the order of reactions in [1]

$$FeO + CO = [Fe] + CO_2, \tag{10'}$$

$$MnO + CO = [Mn] + CO_2, \tag{14'}$$

$$FeO + H_2 = [Fe] + H_2O, \tag{17'}$$

$$MnO + H_2 = [Mn] + H_2O, \tag{21'}$$

$$2FeO + [Si] = 2[Fe] + SiO_2, \tag{24'}$$

$$2MnO + [Si] = 2[Mn] + SiO_2, \tag{28'}$$

$$2.5FeO + [P] = 2.5[Fe] + 0.25P_4O_{10}, \tag{31'}$$

$$2.5MnO + [P] = 2.5[Mn] + 0.25P_4O_{10}, \tag{35'}$$

$$MnO + [Fe] = [Mn] + FeO, \tag{39'}$$

$$FeO + [Ca] = [Fe] + CaO, \tag{40'}$$

$$MnO + [Ca] = [Mn] + CaO, \tag{41'}$$

$$1.5FeO + [Al] = 1.5[Fe] + 0.5Al_2O_3, \tag{42'}$$

$$1.5MnO + [Al] = 1.5[Mn] + 0.5Al_2O_3, \tag{43'}$$

$$2FeO + [C] = 2[Fe] + CO_2, \tag{44'}$$

$$2MnO + [C] = 2[Mn] + CO_2. \tag{45'}$$
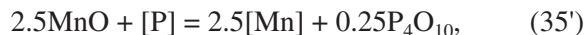
In contrast to reactions with pure materials [1], the change in Gibbs energy for reactions involving dissolved components will be denoted by z_i: $z_i \equiv \Delta G_{i'}$. In Eqs. (1')–(45'), the change in Gibbs energy $\Delta_r G_{i'} \equiv z_i$ is calculated using the Hess law on the basis of $\Delta_r G_1$–$\Delta_r G_{45}$ (Table 1 in [1]) and $\Delta_r G_{46}$ and $\Delta_r G_{59}$ (Table 2 in [1]); we also employ Eqs. (47) and (54)–(59) for the solution processes in Eqs. (46) and (48)–(53). For example, since the reaction in Eq. (1') is evidently the algebraic sum of Eqs. (1.1) and (48), then

$$z_1 \equiv \Delta_r G_{1'} = \Delta_r G_1(\equiv y_1) - \Delta_r G_{48}(\equiv \Delta_r G_{54})$$
$$= y_1 - y_{48}. \tag{60}$$
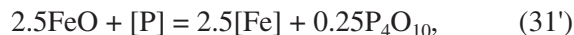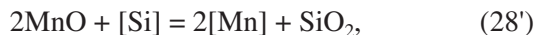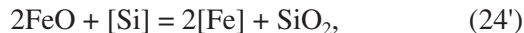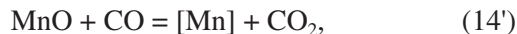
It follows from similar considerations that

$$z_2 \equiv \Delta_r G_{2'} = \Delta_r G_{1.2} - \Delta_r G_{48} = y_2 - y_{48}, \tag{61}$$

$$z_3 \equiv \Delta_r G_{3'} = \Delta_r G_{1.3} + \Delta G_{46} - \Delta G_{48}$$
$$= y_3 + y_{46} - y_{48}, \tag{62}$$

$$z_4 \equiv \Delta_r G_{4'} = \Delta_r G_{1.4} - \Delta G_{48} = y_4 - y_{48}, \tag{63}$$

$$z_5 \equiv \Delta_r G_{5'} = \Delta_r G_{1.5} - \Delta G_{48} = y_5 - y_{48}, \tag{64}$$

$$z_6 = \Delta_r G_{6'} = \Delta_r G_{1.6} - \Delta G_{48} = y_6 - y_{48}, \tag{65}$$

$$z_7 \equiv \Delta_r G_{7'} = \Delta_r G_{1.7} - \Delta G_{48} + \Delta G_{50}$$
$$= y_7 - y_{48} + y_{50}. \tag{66}$$

For reactions involving only the oxides FeO and MnO, the change in Gibbs energy is

$$z_{10} = y_{1.10} + y_{46}, \quad (67)$$

$$z_{14} = y_{1.14} + y_{50}, \quad (68)$$

$$z_{17} = y_{1.17} + y_{46}, \quad (69)$$

$$z_{21} = y_{1.21} + y_{50}, \quad (70)$$

$$z_{24} = y_{1.24} + 2y_{46} - y_{49}, \quad (71)$$

$$z_{28} = y_{1.28} + 2y_{50} - y_{49}, \quad (72)$$

$$z_{31} = y_{1.31} + 2.5y_{46} - y_{51}, \quad (73)$$

$$z_{35} = y_{1.35} + 2.5y_{50} - y_{51}, \quad (74)$$

$$z_{39} = y_{1.39} - y_{48} + y_{50}, \quad (75)$$

$$z_{40} = y_{1.40} + y_{48} - y_{52}, \quad (76)$$

$$z_{41} = y_{1.41} + y_{50} - y_{52}, \quad (77)$$

$$z_{42} = y_{1.42} + 1.5y_{48} - y_{53}, \quad (78)$$

$$z_{43} = y_{1.43} + 1.5y_{50} - y_{53}, \quad (79)$$

$$z_{44} = y_{1.44} + 2y_{46} - y_{48}, \quad (80)$$

$$z_{45} = y_{1.45} + 2y_{50} - y_{48}. \quad (81)$$

For the reduction of iron and manganese from FeO and MnO, we may write linear dependences

$$y_i \equiv \Delta_r G^\circ_{1.i} = A_{1.i} + B_{1.i}T. \quad (82)$$

Table 1 presents the values of $A_{1.i}$ and $B_{1.i}$ calculated in [1].

The temperature dependence of ΔG_i in Eqs. (46) and (48)–(53) may be written in the general form

$$y_i = a_i + b_iT. \quad (83)$$

Table 2 presents the corresponding values of a_i and b. Equations (47) and (54)–(59) are taken from [3].

On that basis, we may calculate z_i for different temperatures (Table 3).

Table 1. Values of $A_{1.i}$ and $B_{1.i}$ in Eq. (82) for various reactions [1]

Eq.	y_i	Value	
		$A_{1.i}$	$B_{1.i}$
(1.3)	y_3	136821	–142.19
(1.7)	y_7	282573	–168.89
(1.10)	y_{10}	–27348	28.57
(1.14)	y_{14}	118403	1.86
(1.17)	y_{17}	1717.3	1.14
(1.21)	y_{21}	147469	–25.56
(1.24)	y_{24}	–375956	66.94
(1.28)	y_{28}	–84452	13.528
(1.31)	y_{31}	–156296	101.03
(1.35)	y_{35}	208084	34.257
(1.39)	y_{39}	145752	–26.708
(1.40)	y_{40}	–417052	72.348
(1.41)	y_{41}	–271300	45.64
(1.42)	y_{42}	–463183	77.282
(1.43)	y_{43}	–244555	37.22
(1.44)	y_{44}	109473	–113.62
(1.45)	y_{45}	400977	–167.03

Table 2. Values of a_i and b_i in Eq. (83) for the solution of elements in liquid iron [3] in Eqs. (46) and (48)–(53) when $x_{Fe} = 0.8$ in Eqs. (47) and (54)–(59)

Eq.	y_i	Values	
		a_i	b_i
(46)	y_{47}	0	–1.86
(48)	y_{54}	22594	–42.31
(49)	y_{55}	–131540	–17.23
(50)	y_{56}	–4078	–38.29
(51)	y_{57}	–122215	–19.15
(52)	y_{58}	–39462	49.38
(53)	y_{59}	–63185	–27.98

ANALYSIS OF THE RESULTS FOR $\Delta_r G_{i'}$

On the basis of Table 3, the calculated values of $\Delta_r G_{i'} = j_i(T)$ for the reduction of iron and manganese from FeO and MnO by components dissolved in liquid iron are analyzed so as to identify the possible change in relative thermodynamic probability of individual reactions in particular series (series of oxides in terms of the degree of oxidation of the metal or series of reducing agents in terms of their reducing properties) in comparison with the reaction of pure components.

General analysis of Table 3 shows that, as for the reaction between pure components, the probability of reduction by a 1% solution of carbon in iron declines on passing from higher to lower oxides of iron and manganese. Moreover, comparison of the ratio of $z_{i'}(T)$ in Table 3 to $y_{1.i} = f_i(T)$ in Table 3 of [1] indicates that they are completely in agreement. In fact, at all the temperatures considered, $y_{1.4} < y_{1.5} < y_{1.1} < y_{1.6} < y_{1.2} < y_{1.3} < y_{1.7}$ and $z_4 < z_5 < z_1 < z_6 < z_2 < z_3 < z_7$.

To establish the relative reduction characteristics of individual processes that involve components dissolved in the liquid metal, we formulate Table 4, with the following transformations: [Al] $\longrightarrow$ AlO$_{1.5}$, [Ca] $\longrightarrow$ CaO, [Si] $\longrightarrow$ SiO$_2$, [C] $\longrightarrow$ CO, [C] $\longrightarrow$ CO$_2$, H$_2$ $\longrightarrow$ H$_2$O, CO $\longrightarrow$ CO$_2$, [P] $\longrightarrow$ PO$_{2.5}$.

Table 3. Calculated values of $\Delta_r G_{i'}^\circ = z_i$ when $i = 1\text{--}45$ for the reduction of iron and manganese from their oxides

T, K	$z_{1'}$	$z_{2'}$	$z_{3'}$	$z_{4'}$	$z_{5'}$	$z_{6'}$	$z_{7'}$	$z_{10'}$
1000	−35805.4	57707	61291	−152957	−37479	−71997	133806.2	5662.66
1100	−53665.9	42356.9	50357.8	−167471	−84627.5	−72075.5	118189.5	8149.38
1200	−72028.5	27759.9	38922.4	−182068	−131860	−71610.1	102279.9	10343.22
1300	−89094.1	12577.1	27738.2	−197041	−142649	−89303.3	86621.3	12704.42
1400	−106913	−2731.14	16846.8	−211094	−155866	−106285	70837.3	15232.98
1500	−124690	−17370	5788	−221340	−168622	−122179	54885.8	17468.66
1600	−142466	−32008.8	−5270.8	−235770	−181796	−137236	37888.4	19704.34
1700	−158863	−50915.3	−14739.6	−248819	−195682	−152377	21016.5	23404.43
1800	−176472	−71035.2	−23748.2	−262662	−209526	−167476	4186.4	27439.23
1900	−197847	−89899.9	−33175.2	−276925	−222114	−183831	−12225.3	31055.63
2000	−229222	−103702	−42560.4	−290727	−235916	−198888	−29013.5	34630.19

T, K	$z_{14'}$	$z_{17'}$	$z_{21'}$	$z_{24'}$	$z_{28'}$	$z_{31'}$	$z_{35'}$	$z_{39'}$
1000	159083.4	8214.9	161636	−154933	−9902.8	224219.3	304375.4	72515.2
1100	164161.6	7689.1	163701	−148979	−13315.4	236221.3	295575	67831.7
1200	169156.2	6786.8	165600	−143443	−16728	247281.9	286356.2	63357.5
1300	174318	6177.4	167791	−137907	−20140.6	258447.1	277242	58883.2
1400	179228.9	5777.1	169773	−131953	−23971.6	270135.3	267604.8	53990.5
1500	183846.8	5251.4	171630	−126417	−28221	281195.9	257340	49097.8
1600	187418.8	4725.6	172440	−120881	−34562.4	292151.9	244355.6	43159.1
1700	190990.8	5664.3	173251	−112416	−40903.8	306768.9	231371.2	35756.1
1800	194479	7063.1	174103	−100186	−44316.4	322327.3	218282.2	27934.6
1900	198385.7	8085.5	175416	−89210.4	−47310.6	336735.1	206134.6	20949.9
2000	201832.2	9107.8	176310	−78653.7	−51560	351142.8	192941	13546.8

T, K	$z_{40'}$	$z_{41'}$	$z_{42'}$	$z_{43'}$	$z_{44'}$	$z_{45'}$
1000	−344634.4	−272119.2	−205359.4	−254960	63243.2	208273.7
1100	−345995.3	−278163.6	−193211.2	−253239	54425.7	190089.1
1200	−346937.9	−283580.4	−181899.8	−252041	44813.1	171528.1
1300	−347671.2	−288788	−170065.3	−250320	35619	153385.4
1400	−347776.9	−293786.4	−158126.3	−249123	26885.1	134866.1
1500	−348510.2	−299412.4	−146501.1	−248239	17691	115886.7
1600	−349243.5	−306084.4	−135085	−249133	8497	94815.18
1700	−348512.5	−312756.4	−121263.2	−249818	2357.1	73869.22
1800	−344434.2	−316499.6	−107023	−250712	−2987.8	52881.42
1900	−335335.1	−314385.2	−93410.33	−250979	−9169.4	32730.42
2000	−326236	−312689.2	−79797.69	−251873	−15351	11742.62

Note that, whereas the first four transformations are characterized by the lowest $\Delta_r G_i$ values, irregular variation in $\Delta_r G_i$ is observed from the transformation $[\text{C}] \longrightarrow \text{CO}_2$ to the end of Table 3. To determine the actual sequence of transformations, we formulate corresponding scores. At each chosen temperature (1200, 1600, and 2000 K) for FeO and MnO (corresponding to the six rows in Table 4), the position M of each transformation in the series in order of increasing $\Delta_r G_{i'}$ is established. Then, for each transformation, the sum of positions ΣM is found, and hence we determine the final position of this transformation in the series with declining reducing characteristics of the components and their transformations (Table 4).

Thus, taking account of the solution of elements in liquid iron, we may rank the transformations in the following sequence in terms of increasing ability to reduce

Table 4. Change in the Gibbs energy $\Delta_r G_i \equiv z_i$ in the reduction of iron and manganese from their oxides FeO and MnO by reducing agents dissolved in hot metal at various temperatures

Oxide being reduced	Change in $\Delta_r G_i \equiv z_i$ in the transformation $nMeO + [V] = n[Me] + VO_n$							
	$[Al] \longrightarrow AlO_{1.5}$		$[Ca] \longrightarrow CaO$		$[Si] \longrightarrow SiO_2$		$[C] \longrightarrow CO$	
	M	z_{40} and z_{41}	M	z_{42} and z_{43}	M	z_{24} and z_{28}	M	z_3 and z_7
				$T = 1200$ K				
FeO	1	–346938	2	–181900	3	–143443	7	38922
MnO	1	–283580	2	–252041	3	–16728	4	102280
				$T = 1600$ K				
FeO	1	–349244	2	–135085	3	–120881	4	–5271
MnO	1	–306084	2	–249133	3	–34562	4	37888
				$T = 2000$ K				
FeO	1	–326236	2	–79798	3	–78654	4	–42560
MnO	1	–312689	2	–251873	3	–51560	4	–29014
ΣM	6		12		18		27	
Final position	I		II		III		IV	

Oxide being reduced	Change in $\Delta_r G_i \equiv z_i$ in the transformation $nMeO + [V] = n[Me] + VO_n$							
	$[C] \longrightarrow CO_2$		$H_2 \longrightarrow H_2O$		$CO \longrightarrow CO_2$		$[P] \longrightarrow PO_{2.5}$	
	M	z_{17} and z_{21}	M	z_{44} and z_{45}	M	z_{10} and z_{14}	M	z_{31} and z_{35}
				$T = 1200$ K				
FeO	4	6787	8	44813	5	10343	6	247282
MnO	5	165600	7	171528	6	169156	8	286356
				$T = 1600$ K				
FeO	5	4726	6	8497	7	19704	8	292152
MnO	6	172440	5	94815	7	187419	8	244356
				$T = 2000$ K				
FeO	6	9108	5	–15351	7	34630	8	351143
MnO	6	176310	5	11743	8	201832	7	192941
ΣM	32		36		40		45	
Final position	V		VI		VII		VIII	

Note: The position M is determined by the reducing properties of the reducing agent V.

the oxides FeO and MnO in the interval 1200–2000 K: $[P] \longrightarrow PO_{2.5}$, $CO \longrightarrow CO_2$, $[C] \longrightarrow CO_2$, $H_2 \longrightarrow H_2O$, $[C] \longrightarrow CO$, $[Si] \longrightarrow SiO_2$, $[Al] \longrightarrow AlO_{1.5}$, $[Ca] \longrightarrow CaO$.

CONCLUSIONS

Comparison of Table 4 with Table 3 in [1] indicates that, when taking account of the solution of elements in liquid iron, we must remember that the reducing properties of calcium are theoretically much higher than those of aluminum. This is confirmed in that $z_{1.40} \equiv \Delta_r G_{1.40} < z_{1.42}$ and $z_{1.41} \equiv \Delta_r G_{1.41} < z_{1.43}$. In terms of reducing properties, the processes $C \longrightarrow CO_2$ and $H_2 \longrightarrow H_2O$ change places (Table 4) so that, when taking account of the solution of reagents in liquid metal,

we must determine the reduction characteristics of individual processes in accordance with Tables 3 and 4.

REFERENCES

1. Zhibinova, I.A., Shakirov, K.M., Protopopov, E.V., and Shakirov, M.K., *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.*, 2007, no. 4, pp. 3–20.

2. Eliott, J.F., Gleiser, M., and Ramakrishna, V., *Thermodynamics for Steel Making*, Reading, Mass.: Addison-Wesley, 1963.

3. Popel, S.I., Sotnikov, A.I., and Boronenkov, V.N., *Teoriya metallurgicheskikh protsessov* (Theory of Metallurgical Processes), Moscow: Metallurgiya, 1986.